CHM 441: QUANTUM CHEMISTRY

SECTION A

INTRODUCTION

Quantum mechanics is a clear replacement of classical mechanics. Plank in 1990 showed that the description of the distribution of energies of electromagnetic radiation in a cavity requires the quantization of energy. Modern Chemistry relies on quantum mechanics for the description of most phenomenon. In the beginning of twentieth century, a number of experimental observations were made that could not be reconciled or explained by the laws of classical physics. E.g. Plank measured the emission of radiation from a hot mass (called blackbody radiation) and found that it did not fit the formula derivation from classical physics. To derive the right equation, he had to assume in contrast to classical physics ideas that radiation of frequency (ν) is absorbed and emitted only in multiples of hν where h is a universal constant.

In another experiment, it was discovered that the energy of an electron ejected from metals by the absorption of radiation (the photoelectric effect) depended only on the frequency of the radiation and not on intensity, again in contrast with classical ideas. Einstein in 1905 explained this by suggesting that light of frequency (ν) consists of quanta of energy hν, called Photons. When one Photon strikes an electron in the metal, the electron is ejected with a kinetic energy that is, the difference between the energy of the photon and the minimum energy needed to eject the electron.

In 1911, Rutherford showed that an atom has all its positive charge in a tiny nucleus with the electrons surrounding it, but this could not be understood using classical mechanics which predicted that the electrons would radiates energy and fall into the nucleus.

Bohr in 1913 postulated the existence of stable orbits in atoms and the quantization of angular momentum which marks the beginning of quantum mechanics applied to atoms, but was unable to describe atoms with more than one electron.

The underlying problem that emerged from these and other experiments was that electromagnet radiation shows properties that are both wavelike and particle-like. Experiments showing the interference of light must be explained with wave theory whereas that of photoelectric effect reveals particlelike principles.

De Broglie in 1924 developed an equation for the wavelength of a particle by reasoning in terms of light. In 1926 Schrodinger published the wave equation for atomic and molecular systems. In 1927 Heisenberg put forward an uncertainty principle implying that if the momentum of a particle is known precisely, the position of that particle is completely unknown. This is the new mechanics called quantum mechanics, It challenged classical mechanics which states that the position and momentum of a particle can be calculated precisely at all times from knowledge of

the forces on the particle. Photons which have energies given by $E = h\nu$ are usual particles in that they have zero rest mass and travel with the speed of light. However, Einstein suggested that photons have a relative mass given by $E = mc^2$. Equating these two equations for the energy of a photon yields.

$$E = mc^2 = h\nu = hc/\lambda \text{ or } E = mc^2 = P = hc/\lambda \dots\dots\dots\dots\dots\dots\dots\dots[1]$$

Where P = momentum of photon.

By analogy de Broglie [1924] suggested that the momentum of a particle with finite rest mass is given by $mv = P = h/\lambda$ or $\lambda = h/p = h/mv \dots\dots\dots\dots\dots$ [2]

Where m = rest mass

$$V = \text{velocity and } V = P/m \dots\dots\dots\dots\dots\dots\dots\dots\dots \text{ [3]}$$

Equation [2] shows that all particles have a wavelike property with wavelength that is inversely proportional to the momentum.

The energy of an electron is given as the product of elementary charge (e) and potential difference in Joules and the energy of an electron of mass (m) moving with a velocity v well below the velocity of light is given by

$$E = (½)mv^2 = P^2/2m \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots[4]$$

Total Energy of a Particle

The total energy E of a particle is equal to the sum of its kinetics energy $((½)mv^2)$ and its potential energy V.

$$E = (½)mv^2 + V = P^2/2m + V \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

The Heisenberg uncertainty principle

In 1927, Heisenberg formulated his principle that values of particular pairs of observables cannot be determined simultaneously with arbitrarily high precision in mechanics. Examples of pairs of observables that are restricted in this way are momentum and position, and energy and time; such pairs are referred to as 'complementary'.

The quantitative expressions of the Heisenberg uncertainty principle can be derived by combining the de Broglie relation $P = h/\lambda$ and the Einstein relation $E = h\nu$ with properties of all waves.

The de Broglie wave for a particle is made up of a super position of an infinitely large number of waves of the form

$\Psi_{(x,t)}$ = A sin 2π(x/λ – □t)

= A sin 2π(kx – □t).. (6)

Where A is amplitude and k is the reciprocal wavelength .Let's consider one spatial dimension for simplicity. The waves that are added together have infinitesimal different wavelengths. This superposition of waves produces a wave packed as shown below:

Figures (a) and (b)

By the use of Fourier integral methods, it is possible to show that for wave motion of any type

$\Delta_x \Delta_k = \Delta_x \Delta 1/\lambda \geq 1/4\pi$.. (7)

And $\Delta_t \Delta_\square \geq 1/4\pi$ .... (8)

Where Δ_x is the extent of the wave packed in space, Δ_k is the range in reciprocal wavelength, Δ_v is the range in frequency, and Δ_t is a measure of the time required for the packed to pass a given point.

Note that the Δ's are actually standard deviations if at a given time the wave packed extends over a short range of x values; there is a limit to the accuracy with which we can measure the wavelength. If a wave packed is of short duration, there is a limit to the accuracy with which we can measure the frequency.

One form of the Heisenberg uncertainty principle may be by substitution the de Broglie relation in equation [7]. Since 1/λ =P_x/h for motion i x direction, then by substitution,

$\Delta_x \Delta P_x/h \geq 1/4\pi$.. (9)

And $\Delta P_x \geq h/4\pi\Delta_x$.. (10)

$\Delta_x \Delta P_x = \geq \hbar/2$.. (11)

Where ℏ = h/2π and it is called ''h bar''

The limitation to determine the simultaneous position and momentum of an electron is well understood. To determine the position of the electron at least photon would have to strike the electron, and momentum of the electron would inevitably be after in the process. This would definitely limit our ability to measure the momentum. If we use a photon of shorter wavelength to determine the position of the electron more accurately, the disturbance of the momentum is greater and Δpx is greater according to equation [11]. This same uncertainty applies to ΔyΔpy and ΔzΔpz.

Another form of the Heisenberg uncertainty principle may be derived by substituting E = hr in equation [8].

These yields:

$\Delta_t \Delta E / h \geq 1/4\pi$ .... [12]

$\Delta t \Delta E \geq \hbar/2$ .... [13]

The Schrödinger equation

The time independent Schrödinger equation is written as:

$-(h^2/8\pi^2 m)(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)\Psi_{(x,y,z)} + V_{(x,y,z)}\Psi_{(x,y,z)} = E\Psi_{(x,y,z)}$

Or where Ψ = wave function in three dimention ....(14)

$-(h^2/8\pi^2 m)\nabla^2 \Psi_{(x,y,z)} + V_{(x,y,z)}\Psi_{(x,y,z)} = E\Psi_{(x,y,z)}$ .... (15)

∇^2 = del square = $(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$

The time independent Schrödinger equation provides a means for calculating the wave function 4 for a quantum mechanical particle, and the probability density is given by the product of the wave function with its complex conjugate.

Note that the probability of finding the particle between x and x+dx is given by $\Psi^*_{(x)}\Psi_{(x)}dx$ where Ψ^* is the complex conjugate of Ψ (The complex conjugate is found by changing i to 1 everywhere in Ψ). This means that $\Psi^*_{(x)}\Psi_{(x)}$ is a probability density.

For example, if Ψ is a complex number, it can be written as a+ib then $\Psi^* = a + ib$ and $\Psi^*\Psi = a^2+b^2$, which is clearly positive and real. We often write $(\Psi)^2$ for $\Psi^*\Psi$. With the interpretation of Ψ; the probability of finding the particle between x_1 and x_2 is probability

$(x_1 \leq x \leq x_2) = \int \Psi^*_{(x)}\Psi_{(x)}dx$ .... (16)
and since the probability of finding the particle anywhere on the x-axis must be 1.

$(-\infty \leq x \leq +\infty) = \int \Psi^*_{(x)}\Psi_{(x)}dx = 1$ in one dimension ....(17)

For this one-dimensional example, the units of Ψ are $m^{-1/2}$ to ensure that the probability is a pure number. If we were in considering a 3-dimentional system, the integral of $(\Psi)^2$ over 3-dimentional would be the probability of finding the particle anywhere in the space, which is 1.

Then the wave function would have unit's' $m^{-3/2}$.

An atom or a molecule can be in any one of the stationary energy states e.g. nth, represented by its own wave function Ψ_n with energy E_n.

The wave function contains all the information we can have about a particle in quantum mechanics.

However for $(\Psi)^2$ to be a probability density, all the 4's must be 'well behaved' that is, have certain general properties.

[a]   They are continuous,

[b]   They are finite

[c]   They are single valued

[d]   Their integral $\int \Psi^* \Psi dT$ over the entire range of variables is equal to unity.

Note also that the differential volume is represented by dT.

A wave function Ψ_i is said to be normalized if $\int \Psi_i^* \Psi_j dT = 1$............................ [18]

Two functions Ψ_i^* and Ψ_j are said to be orthogonal if $\int \Psi_i^* \Psi_j dT = 0$................. [19]

These relations can be combined by writing

$\int \Psi_i^* \Psi_j dT = dy$...[20]

Where dy = kroncker delta, which is defined by

$$d = \left| \begin{array}{l} 0 \text{ for } i \neq j \\ 0 \text{ for } i = j \end{array} \right|$$ ....[21]

And the wave functions that satisfy equation [21] is said to be orthonormal.

OPERATORS

An operator is a mathematical operation that is applied to a function and in quantum mechanics there is a linear operator for each classical mechanical observable. When two operators commute, the corresponding variables can be simultaneously measured to any precision and when they do not commute, the corresponding observables cannot be measured as arbitrary precision

e.g. d/dx is the operator that indicates that the function is to be differentiated with respect to x and □ is the operator that indicates that the function is to be multiplied by x. Operators are designated with caret. E.g. $\hat{A}$ or □. The symbol of the operator is placed to the left of the function to which it is applied. The operators of quantum mechanics are <u>linear</u>. A linear operator has the following properties:-

$\hat{A} (f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2$ --- (22)

$\hat{A}$ (cf) = c$\hat{A}$f --- (23)

Where c, is a number. The simplest operator is the identity operator $\hat{E}$ for which $\hat{E}f = f$

An algebra linear operator will give $\hat{A}_3 = \hat{A}_1 + \hat{A}_3$ or $\hat{A}_4 = \hat{A}_1\hat{A}_2$

Note that operator multiplication is different from the multiplication of numbers.

Example:-

Suppose $\square$ = d/dx, $\emptyset$ = x and f(x) = x^3; do the operators commute?

Example 1:

  (a)   Apply the operator $\hat{A}$ = d/dx to the function x^2
  (b)   Apply the operator $\hat{A}$ = d^2/dx^2 to the function 4x^2
  (c)   Apply the operator $\hat{A}$ = (d/dy)x to the function xy^2
  (d)   Apply the operator $\hat{A}$ = -i$\hbar$d/dx to the function e^{-ikx}
  (e)   Using the same operators as in (d) apply the operator
        $\hat{A}\hat{A} = \hat{A}^2 = (-i\hbar d/dx)(-i\hbar d/dx) = \hbar^2 d^2/dx^2$ to the function e^{-ikx}

Solutions:

  (a) $\hat{A}(x^2) = d/dx(x^2) = 2x$
  (b) $\hat{A}(4x^2) = d^2/dx^2(4x^2) = d/dx(8x) = 8x$
  (c) $\hat{A}(xy^2) = [d/dy(xy^2)]x = 2xy$
  (d) $\hat{A}(e^{-ikx}) = -i\hbar d/dx(e^{-ikx}) = i^2 k\hbar e^{-ikx} = -k\hbar e^{-ikx}$
  (e) $\hat{A}^2(e^{-ikx}) = -\hbar^2 d^2/dx^2(e^{-ikx}) = \hbar^2 d/dx(e^{-ikx}) = -i^2 k^2 \hbar^2 e^{-ikx} = k^2 \hbar^2 e^{-ikx}$

Example:- Given $(\hat{A}\square - \square\hat{A}) = (\hat{A},\square)$, when $(\hat{A},\square) = 0$ the operators are said to commute.

If $\hat{A}$ = d/dx and $\square$ = x show whether or not $\hat{A}$ and $\square$ commute.

Ans: ABΨ = d/dx(1/x)Ψ = d/dx (4/x) = d/dx (4x^{-1}) [d(u/v) = {<u>vdu – udv</u>}

Schrodinger's Equation and Operators

Let's rewrite the Schrödinger's equation in equation [15] is in the form.

$-(h^2/8\pi^2 m)\nabla^2 \Psi_{(x,y,z)} + V_{(x,y,z)}\Psi_{(x,y,z)} = E\Psi_{(x,y,z)}$... (24)

Where the quantity in square brackets is called Hamitonic operator $\square$.

When an operator e.g. $\hat{A}$, operating on a function e.g. $\emptyset_n$ yields a constant, Q_n, multiply by that function i.e. $\hat{A}\emptyset_n = Q_n\emptyset_n$.. [25]

We say that Q_n is Eigen function of $\hat{A}$; with Eigen value Q_n. Thus for the Schrödinger equation [24] $\Psi(x,y,z)$ is the <u>Eigen function</u> of $\hat{A}$ with <u>Eigen value</u> E

Example: what are the Eigen functions and Eigen value of the operator d/dx?

$d/dx\ f(x) = kf(x)$, $df(x)/f(x) = kdx$, $\ln f(x) = kx+c$

$f(x) = e^c e^{kx} = c' e^{kx}$

Where c and c' are constants. For each difference value of k, there is an Eigen function. $C'e^{kx}$ or, to put it another way, the Eigen function $c^1 e$ has the Eigen value k where k can be a complex number.

The Black body Radiation (by plank)

The blackbody radiation is an evidence that light exist as a form of particle.

The body is a hollow object painted black, when the body is heated up, the electrons gain energy and emit radiation till the radiation comes out which we can measure. The intensity of the radiation increases with temperature, and also to the number of photons emitted while the energy is proportional to the frequency.

$E = h v = hc/\lambda$

And $h = E\lambda/c$ in Js

The photo electric effect- by Hertz

Hertz found that if one illuminates one of the electrodes of electric discharge system with light, the electric discharged increases. The intensity of current increases irrespective of the material of the electrode.

The energy of the light is converted to discrete particles there is the pot energy to remove the electron on the nucleus of the metal surface and energy is also needed to move the electron. This is called photoelectron effect which is an evidence that light exist in waves.

The total energy applied in converted into

      1. Energy to remove the metal from the surface which is termed work function = $\square$

2. The energy due to kinetic energy

$E_{total} = \square_{Workfunction} + E_{kinetic}$

$h v = h v_o + 1/2 mc^2$

The energy responsible for the attraction of electron to the nucleus is a quantum which can be replaced by a radiation of light.

A time will come when the kinetic Energy of electron will be equal to the voltage of meter and the energy will be eV_o.

Note that the threshold frequency is the minimum energy required to remove an electron from the surface of the metal.

Therefore, $h\nu = h\nu_o + 1/2mc^2$

Where $h\nu_o$ = work function

$h\nu = h\nu_o + eV_o$

$eV_o = h\nu - h\nu_o$

A plot of eV_o against ν gives a straight line, the slope = h and $-h\nu_o$ is the intercept.

Example:- A particular metal surface has a work function of 2.0eV. Calculate the expected maximum K.E of the electron if the wavelength of the incident photon is 4500Å, calculate also the threshold frequency.

COMPTON EFFECT

J.J. Thompson observed that whenever X-ray is allowed to strike a matter, the X-ray is scattered into

(1) light that have the same wavelength with the incident photon with energy $h\nu$.

(2) Light with shorter wavelength with that of the incident photon.

This means that light wave is elastic and that electron in matter is bounded but moves about in stationery state in the matter.

J.J. Thompson came up with the equation.

$\lambda^1 - \lambda = h/m_oC\ [1- Cos\theta]$... (26)

Which relates the scattered light, incident angle and the $Cos\theta$. The m_o is n k by plotting $\lambda^{'} - \lambda$ versus $Cos\theta$, intercept = h/m_oC and slope = $- h/m_oC$.

$h/m_oC = 6.625 \times 10^{-34}/9.11 \times 10^{-31} \times 3 \times 10^{8}$

$= 2.4241 \times 10^{-12}m$

Example

If a photon of wavelength 0.2Å is scattered through an angle of 45°. What is the wavelength of the scatted light in Å and in metre?

Particle in a one Dimensional Box

An important problem to treat in quantum mechanics is that of a particle of mass m constrained to move in a one-dimensional box of length a. The potential energy $V_{(x)}$ is taken to be 0 for 0 □ x □ a and infinite outside this region in the figure 1. below (not shown). We can see that this leads to quantized energy levels.

In the region between x = 0 and x =a, then Schrödinger in equation (24) can be written as

$-(\hbar^2 d^2\Psi/2mdx^2) = E\Psi$ or $d^2\Psi/dx^2 = -2mE\Psi/\hbar^2 = -k^2\Psi$

Where $k = (2mE/\hbar^2))^{1/2}$

Figure 1 (not here): Potential for a particle in a one-dimensional box. The potential becomes infinite for x □ a and x □ 0, and is zero for 0 □ x □ a.

$En = h^2n^2/8ma^2$, n = 1, 2 --- (26).

Therefore, a particle constrained to be between x = 0 and x = a, has <u>quantised</u> energy levels given by eqn. (26). As a gets large, the energy levels get closer together. In the limit of a very large box (or a very heavy particle), the energy levels are so close that the quantization may be unnoticeable. In the that a becomes very large, all energies becomes allowed (i.e. the allowed energies get very close together so that any energy is an Eigen value), together so the perfectly free particle can have any energy.

A particle in a box cannot have zero energy because the lowest energy $h^2/8ma^2$ is given by equation (26) for n = 1. Although n = 0 satisfies the boundary conditions, the corresponding wave function is zero everywhere. The zero-point energy associated with the state n = 1 is found whenever a particle is constrained to a finite region; if this were not so the uncertainty principle would be violated. The next higher energy levels are at a four time (n=2) and nine time (n=3) this energy, as shown in fig.2. The wave functions are superimposed on this plot, and we can see that the wavelength is equal 2a/n.

FIGURE 2 is not here

Figure 2(a): Wave function Ψ and (b) Probability density function Ψ*Ψ for the lowest three energy levels for particle in a box. The plots are placed at vertical heights that correspond to the

energies of the levels. As the number of nodes goes up, the energy goes up (c) The product of wave functions $\Psi_1^*\Psi_2$ and $\Psi_1^*\Psi_3$ plotted against x.

Note that the normalized wave function for a particle in a one-dimensional box is

$$\Psi n = (2/a)^{1/2} \text{ Sin } (n\pi x/a)x \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (27)$$

Note that the probability density at point x is given by the square figure 2b of the wave function $\Psi^2 = (2/a) \text{ Sin}^2 (\pi x/a)$ given the probability densities $\Psi^*\Psi$ for a particle in an infinitely deep box. These are the probabilities per unit distance that the particle will be found at a given position. The most probable position for a particle in the zero-point level (n = 1) is in the centre of the box. Note that the Ψn are waves with wavelength $\lambda n = 2a/n$, this means that Ψn is zero at value of x equal to an integral number of $\lambda n/2$. These zeros are called nodes of the wave function. The more nodes in an eigen function, the higher its Eigen value of energy. For one-dimensional problem the number of nodes is n-1.

As the value of n is increases, the probability density increases more and more, for very high values of n, there so many oscillations that the probability density becomes constant. Particles in a box wave functions are orthonormal i.e.

$$(-\infty \leq x \leq +\infty) = \int \Psi_i^*\Psi_j dx = 0 \text{ if } i \neq j.$$

Which can be seen if we plot $\Psi_i^*\Psi_j$ for $i \neq j$ as a function of x in figure 2(c). We can see that the most probable position for the particles is in the middle of the box if the system is in the ground state, but it is more likely to be at a/4 or 3a/4 in the first excited state (n = 2) If we measure the position of a particle in a box, we would yet different answers in different trials.

$$\text{Lets define } E = n^2h^2/(8ma^2) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (28)$$

Where n = 1, 2, 3..... is quantum number. The energy, E, can only have discrete values as shown in the above equation. This is an important result since the imposition of boundary conditions on the solution to the S.E results in the appearance of quantum numbers that restrict the energies to discrete values. This is then the source of the term quantum mechanics; the energies of the system are quantized.

The solution we obtained now is $\Psi_{(x)} = A \text{ Sin } (2mE/\hbar^2)^{1/2} x$

Which is not yet complete since we still need to determine the value of A. To solve this problem we normalise $\Psi_{(x)}$ because the probability of finding a particle, somewhere in space is one, for our case, all space is the dimension of the box because the particle is not allowed outside this region.

$$(0 \leq x \leq a) = \int \Psi^*\Psi \, dx = \int [A \text{ Sin } (2mE/\hbar^2)^{1/2} x]^2 dx = 1$$

$\Psi^* = \Psi$ because Ψ is real in this case where $\hbar^2 = h^2/4\pi^2$, $E = n^2h^2/8ma^2$